

Electronic Supplementary Information

Electrochemical and electrical characteristics of ball milled Cs₂Ti₆O₁₃ modified by the surface-to-bulk migration of hydroxyl groups

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Characterization

X-ray diffraction (XRD) measurements were performed on a Rigaku, DMAX 2200/Ultima+ diffractometer (Cu K α radiation, 40 kV, 30 mA). The powder was mixed with a small amount of LaB₆ as the internal standard for unit cell parameters determination, which was refined by CellCalc¹ at $2\theta = 5-50^\circ$. Raman spectra were recorded using a DXR Smart Raman (Thermo Scientific) with laser wavelength of 532 nm and the laser power of 5 mW. IR spectra were recorded in the attenuated total reflectance (ATR) mode using a PerkinElmer, Spectrum 2 instrument. Thermogravimetric analysis (TGA) was performed under the flow of N₂ gas (20 mL·min⁻¹) from RT to 800 °C (10 °C·min⁻¹) using a Perkin-Elmer, Pyris-1 instrument. Solid state ¹H NMR spectra were obtained using a JEOL JNM-ECZ400R/S1 spectrometer. The specific surface area S_{BET} was measured by an Autosorb-1C instrument (Quantachrome) after degassing at 300 °C. The microstructure and elemental composition were characterized using a scanning electron microscope (SEM; JEOL JSM-840A) equipped with an energy-dispersive X-ray (EDX) analyzer. X-ray photoelectron spectroscopy (XPS) measurements were conducted at the SUT-NANOTECH-SLRI XPS workstation (PHI 5000 VersaProbe II, monochromatized Al K α radiation at 1486.6 eV), with the binding energies calibrated to C 1s at 284.8 eV. The analysis area is 300 × 300 μm^2 .

Particle size and zeta potential of the samples were measured by dynamic light scattering (DLS) using a DelsaTM Nano Particle Size Analyzer (Beckman Coulter). An amount of 2-4 mg of the titanate and 3 mL of deionized water (pH 6) was loaded into a quartz cuvette followed by sonication for 300 s. The cuvette was then immediately taken to the instrument. A typical set up is the temperature of 25 °C, repetition number of 15, and the accumulation time 30 s.

Table S1 Summary of the unit cell parameters of the Cs₂Ti₆O₁₃ samples

Sample	$a/\text{Å}$	$b/\text{Å}$	$c/\text{Å}$	Ref.
As made	3.815(3)	17.42(2)	2.967(6)	This work
Ball milled	3.815(2)	17.45(7)	2.961(4)	This work
As made	3.825(2)	17.271(7)	2.961(1)	Grey et al ²

The unit cell parameters of Cs₂Ti₆O₁₃ are practically similar between as made and ball milled samples. However, the observed a -parameter is smaller and the b -parameter is longer than the values first reported by Grey et al.² This might be explained by a small variation in actual stoichiometry between different laboratories.

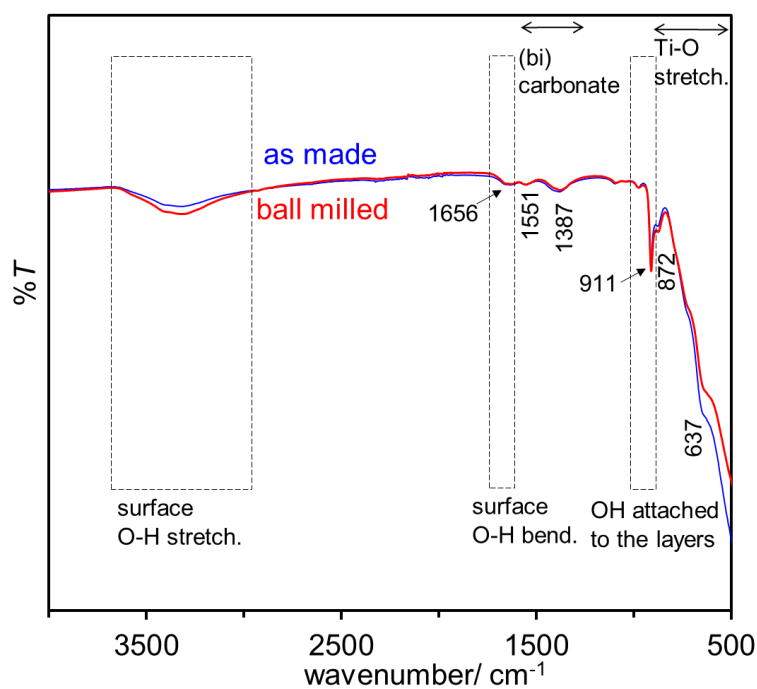


Figure S1. IR spectra of as made and ball milled $\text{Cs}_2\text{Ti}_6\text{O}_{13}$.

We observed the bands due to the lattice vibration of TiO_6 (637, 872 cm^{-1}), surface carbonates/bicarbonates (1387, 1551 cm^{-1}), O-H bending (1656 cm^{-1}) and O-H stretching (~ 3250 cm^{-1}).³⁻⁷ Most importantly, the sharp peak at 911 cm^{-1} is visible which is typically assigned to the OH group directly attached to the layer as opposed to the surface.³⁻⁷ The increased water concentration in the ball milled sample can also be inferred from the relative peak intensity. After ball milling, the Ti-O lattice vibration at 911 cm^{-1} is weaker, but the O-H stretching at 3295-3313 cm^{-1} is stronger. (The spectra were normalized to have the same intensity of the 911 cm^{-1} -peak.) This simple comparison further supports the increasing surface hydroxyl groups induced by the soft vibratory ball milling. It is also consistent with the increased intensity of the band due to OH groups in the Raman spectra.

Table S2 Water content in lepidocrocite-type alkali titanates reported in the literature.

Composition	Treatment	<i>n</i>	Wt% water	Ref.
$\text{Cs}_2\text{Ti}_6\text{O}_{13}\cdot n\text{H}_2\text{O}$	As made	1.79	4.20	This work
$\text{Cs}_2\text{Ti}_6\text{O}_{13}\cdot n\text{H}_2\text{O}$	Ball milled 2 h	1.87	4.39	This work
$\text{Cs}_{0.7}\text{Zn}_{0.35}\text{Ti}_{1.65}\text{O}_4\cdot n\text{H}_2\text{O}$	As made	1.1	7.3	Maluangnont et al ⁸
$\text{Cs}_{0.7}\text{Zn}_{0.35}\text{Ti}_{1.65}\text{O}_4\cdot n\text{H}_2\text{O}$	Ball milled 2 h	0.8	5.3	Maluangnont et al ⁸
$\text{Cs}_{0.7}\text{Zn}_{0.35}\text{Ti}_{1.65}\text{O}_4\cdot n\text{H}_2\text{O}$	Sintered 1100 °C 4 h	0.03	2.26	Sriphan et al ⁹
$\text{K}_{0.8}\text{Zn}_{0.4}\text{Ti}_{1.6}\text{O}_4\cdot n\text{H}_2\text{O}$	As made	0.66	5.5	Maluangnont et al ^{10, 11}

The presence of physisorbed water can be deduced from the mass loss at the temperature less than 300 °C.⁸⁻¹¹ In the examples in Table S2, the XRD patterns are typical of the respective composition, without interlayer expansion due to intercalated water.

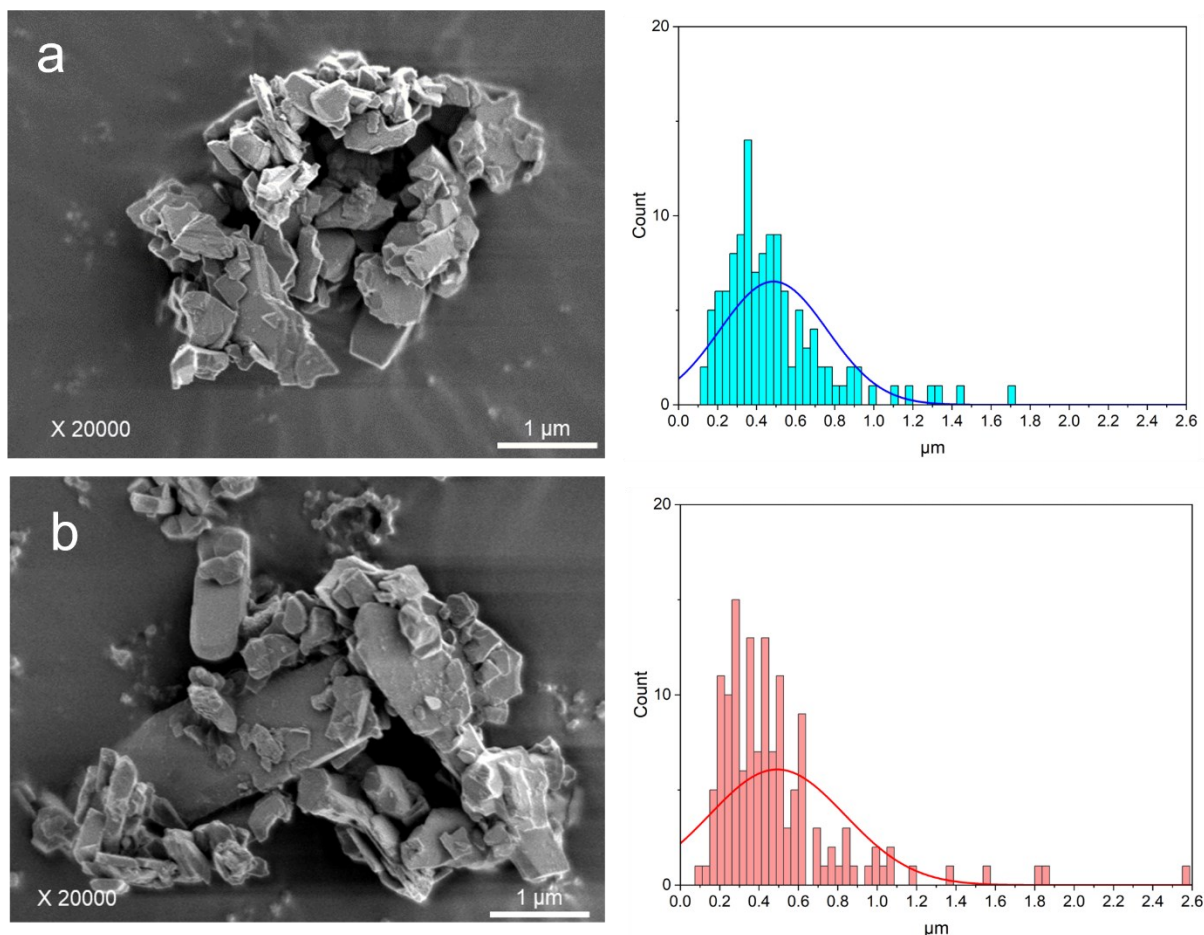


Figure S2 A representative SEM image and the histogram of size distribution of (a) as made, and (b) ball milled $\text{Cs}_2\text{Ti}_6\text{O}_{13}$.

From the image at 20,000 \times magnification, the lateral size of as made $\text{Cs}_2\text{Ti}_6\text{O}_{13}$ is 0.487 μm (number of particle, $N = 120$). This is practically identical to that of the ball milled $\text{Cs}_2\text{Ti}_6\text{O}_{13}$ of 0.493 μm ($N = 140$). Accordingly, there is no significant change to the particle size or the distribution due to ball milling.

Supplementary references

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